Supporting Information

General Methods: All starting materials used were obtained from Sigma-Aldrich, Fluka or TCI America and were used without further purification unless otherwise noted. Thin layer chromatography (TLC) was performed on Sigma-Aldrich TLC Plates (silica gel on aluminum, 200 mm layer thickness, 2-25 mm particle size, 60 Å pore size). The synthesis of monomers **3, 4**, **8a-g, 17** was reported earlier[2i,7,8,9]. The dimers **11** and **14a-c** were prepared according to the reported procedures[8,9]. Column chromatography was performed using silica gel (230-400 mesh) from Solvent technologies.^{1}H nuclear magnetic resonance spectra were recorded either at 400 MHz on Bruker Avance DPX-400 instrument or at 500 MHz on DPX-500 spectrometer at room temperature; ^{13}C NMR spectra were recorded on the same instruments at either 100 or 125 MHz, respectively. ^{1}H and ^{13}C chemical shifts are reported in parts per million relative to the corresponding residual solvent peak. High-resolution Fourier transform mass spectra (FT-ICR MS) were obtained from the W. M. Keck Biotechnology Resource Laboratory at Yale University. Secondary electron images (SEI) were collected with the SEM system on the JEOL JXA-8530F (field-emission-gun, FEG) electron microprobe in the Yale University Department of Geology and Geophysics. The samples of NO_2-(**6**) and NH_2-(**7**) dimers were mounted on double-stick carbon tape, then were coated with conductive carbon or gold to minimize charge buildup and heating of the sample from the electron beam, a requisite for both imaging and compositional analysis under high vacuum. All images were collected at an accelerating voltage of 15 kV and a beam current between 5 nA and 500 pA.

X-ray crystal structures were obtained on Rigaku R-AXIS RAPID imaging plate diffractometer using multi-layer mirror monochromated Cu-Kα radiation. The structure of dimer **7** and was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Although the molecule of trimer **9f** is fully resolved, the refinement is plagued by a severely disordered $CHCl_3$ molecule and thus we can only use this data to confirm atom identity and connectivity. All calculations were performed using the CrystalStructure crystallographic software package[11] except for refinement, which was performed using SHELXL-97[12]. Crystallographic data for dimer **7** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 843052). Structure: $C_{28}H_{39}N_3O_7$, M = 529.63, monoclinic, a = 8.1041(15), b = 22.4088(4), c = 15.8783(3) Å, β = 105.8771(8)^{o}, U = 2773.54(9) Å^3, μ = 7.502 cm^{-1}, T = -180±1^{o}C, space group P2$_1$/c (#14), Z = 4, GOF = 1.075, final R-indices (R_1 = 0.0514, ωR_2=0.1442), 4981 reflections collected, crystal size 0.30 x 0.15 x 0.15 mm.

Crystallographic data of dimer **14a** (CCDC 851714): Structure: $C_{21}H_{26}N_2O_5$, M = 386.45, monoclinic, a = 7.28347(15), b = 21.3595(4), c = 12.9832(9) Å, β = 94.065(7)^{o}, U = 2014.73(15) Å^3, μ = 7.504 cm^{-1}, T = -180^{o}C, space group P2$_1$/n (#14), Z = 4, GOF = 1.116, final R-indices (R_1 = 0.0455, ωR_2=0.1355), 3628 reflections collected, crystal size 0.25 x 0.10 x 0.10 mm.

Crystallographic data of dimer **14c** (CCDC 851713): Structure: $C_{27}H_{38}N_2O_5$, *M* = 470.61, monoclinic, *a* = 26.2228(5), *b* = 7.12522(13), *c* = 29.983(2) Å, β = 111.349(8)°, *U* = 5217.7(5) Å^3, μ = 6.634 cm^{-1}, *T* = -180°C, space group C2/c (#15), *Z* = 8, GOF = 1.068, final *R*-indices (R_1 = 0.0450, ωR_2=0.1226), 4366 reflections collected, crystal size 0.10 x 0.08 x 0.08 mm.
Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)

Synthesis of Me-ester 1:
A round bottom flask was charged with methyl 3-hydroxy-4-nitrobenzoate (0.3 g, 1.5 mmol), 4-(Boc-amino)butyl bromide (0.5 g, 2 mmol) and potassium carbonate (0.3 g, 2.2 mmol) under an atmosphere of nitrogen. The mixture was heated for 2 days in DMF (5 mL) at 70°C then allowed to cool, diluted with distilled water and extracted with ethyl acetate. The combined organic layers were washed with water followed by brine. The organic layer was then dried over Na_2SO_4, filtered and concentrated *in vacuo*.
The resulting oily residue was subjected to silica gel column chromatography (dichloromethane/ethyl acetate, 1:1 mixture as an eluent). Yield 0.35 g (62%).^{1}H-NMR (500 Hz, $CDCl_3$, δ): 1.37 (s, 9H, Boc), 1.61-1.67 (m, 2H, CH_2), 1.79-1.84 (m, 2H, CH_2), 3.11-3.15 (m, 2H, CH_2), 3.89 (s, 3H, COOMe), 4.10 (t, *J* = 6.8 Hz, 2H, OC$\underline{H_2}$CH_2), 4.60 (s, 1H, $\underline{NH}$Boc), 7.59-7.76 (m, 3H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.1, 26.5, 28.4, 39.9, 52.8, 69.4, 79.1, 115.4, 121.3, 125.2, 134.8, 142.5, 151.8, 156.0, 165.2. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{17}H_{24}N_2O_7$ (m/z = 369.1656). Observed m/z = 369.1659. MALDI-TOF, M = $C_{17}H_{24}N_2O_7$ ($[M]^+$, m/z = 368.16).
Hydrolysis of the aryl carboxylic acid Me-ester 1:
A solution of LiOH (0.12 g, 5 mmol) in distilled water (50 mL) was added at 0°C (ice bath) to the methyl-ester **1** (0.9 g, 2.4 mmol) dissolved in 50 mL of THF. The mixture was vigorously stirred for 2 hr at room temperature and then concentrated to approximately 20 mL *in vacuo*. Water (30 mL) was added, the solution was cooled to 0°C and 50 mL of 0.1 M HCl were added under vigorous stirring. Precipitated white deposit was filtered off, washed with water and dried to give 0.52 g (60%) yield of corresponding aryl carboxylic acid **3**[2i]. This material was used in subsequent coupling reactions without further purification.

General protocol for the reduction of nitro functionality into the corresponding amine:
Nitro oligomer (5 mmol, either **1** or **6**, or **18**) was dissolved in a dichloromethane/ethyl acetate mixture (1:5) (50 mL). Palladium on carbon (0.5 g) was added and the reaction mixture was stirred under 1 atm of hydrogen overnight. The reaction suspension was filtered through Celite and the solvent evaporated *in vacuo* to give the corresponding aryl amines (**2**, **7**, **19**) in the nearly quantitative yield. These compounds were used in subsequent coupling reactions without further purification. The synthesis of NH_2-dimers **14a-c** was accomplished following the general procedure for reduction given above from the corresponding NO_2-dimers described in our previous communication[9].
Compound 2: yield 95%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 1.48 (s, 9H, Boc), 1.69-1.75 (m, 2H, CH_2), 1.86-1.92 (m, 2H, CH_2), 3.22-3.27 (m, 2H, CH_2), 3.89 (s, 3H, COOMe), 4.08 (t, *J* = 6.3 Hz, 2H, OC$\underline{H_2}$CH_2), 4.28 (s, 2H, NH_2), 4.63 (s, 1H, $\underline{NH}$Boc), 6.68-7.58 (m, 3H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.5, 27.0, 28.5, 40.4, 51.7, 67.9, 79.3, 112.1, 113.2, 119.4, 124.1, 141.2, 145.3, 156.0, 167.3. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{17}H_{26}N_2O_5$ (m/z = 339.1915). Observed m/z = 339.1916. MALDI-TOF, M = $C_{17}H_{26}N_2O_5$ ($[M + H]^+$, m/z = 339.27).

Compound 7: yield 95%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.05 (d, *J* = 6.8 Hz, 6H, Me_{isobut}), 1.39 (s, 9H, Boc), 1.55-1.62 (m, 2H, CH_2), 1.73-1.80 (m, 2H, CH_2), 2.11-2.19 (m, 1H, $CH_2C\underline{H}Me_2$), 2.99-3.04 (m, 2H, CH_2), 3.86 (s, 3H, COOMe), 3.93 (d, *J* = 8.0 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.01 (t, *J* = 5.6 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 5.52 (s, 2H, NH_2), 6.84-6.87 (m, 1H, NHBoc), 6.70-8.30 (m, 6H, ArH), 9.02 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6): δ 19.0, 26.1, 27.8, 28.3, 52.0, 67.6, 74.5, 77.4, 110.0, 111.7, 112.3, 119.9, 120.6, 121.3, 122.3, 124.5, 132.6, 142.4, 144.6, 148.2, 155.6, 164.5, 165.9. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{28}H_{39}N_3O_7$ (m/z = 530.2861). Observed m/z = 530.2861. MALDI-TOF, M = $C_{28}H_{39}N_3O_7$ ($[M]^+$, m/z = 529.36).

Compound 19: yield 74%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.38-1.40 (m, 15H, Boc + $Me_{isoprop}$), 1.56-1.63 (m, 2H, CH_2), 1.74-1.81 (m, 2H, CH_2), 2.99-3.04 (m, 2H, CH_2), 3.86 (s, 3H, COOMe), 4.03 (t, *J* = 6.4 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 4.72-4.81 (m, 1H, $OC\underline{H}Me_2$), 5.54 (s, 2H, NH_2), 6.72-8.34 (m, 6H, ArH), 6.86-6.89 (m, 1H, NHBoc), 8.99 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.3, 26.5, 27.1, 28.5, 40.4, 52.1, 68.1, 71.7, 110.8, 113.1, 113.4, 118.4, 119.9, 123.4, 124.1, 124.4, 133.6, 140.5, 145.6, 146.1, 156.0, 165.1, 166.9. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{27}H_{37}N_3O_7$ (m/z = 516.2704). Observed m/z = 516.2678. MALDI-TOF, M = $C_{27}H_{37}N_3O_7$ ($[M]^+$, m/z = 515.11).

Compound 14c: ^{1}H-NMR (400 Hz, DMSO-d6, δ): 0.89-0.94 (m, 12H, CH_3), 1.41-1.56 (m, 8H, $CH(C\underline{H}_2Me)_2$), 1.66-1.78 (m, 2H, $OCH_2C\underline{H}Et_2$), 3.86 (s, 3H, COOMe), 3.92 (d, *J* = 6.0 Hz, 2H, $OC\underline{H}_2CHEt_2$), 4.05 (d, *J* = 6.0 Hz, 2H, $OC\underline{H}_2CHEt_2$), 5.48 (s, 2H, NH_2), 6.71-8.32 (m, 6H, ArH), 8.97 (s, 1H, NHCO). ^{13}C NMR (400 Hz, DMSO-d6, δ): 10.9, 11.0, 22.8, 23.0, 69.5, 70.2, 109.6, 111.6, 112.2, 119.8, 120.6, 121.3, 122.3, 124.5, 132.6, 142.3, 144.8, 148.2, 164.5, 165.9. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{27}H_{38}N_2O_5$ (m/z = 471.2854). Observed m/z = 471.2839. MALDI-TOF, M = $C_{27}H_{38}N_2O_5$ ($[M]^+$, m/z = 470.07).

Spectral properties of **14a,b** were described earlier[8,9].

General protocol for an amide coupling in the presence of Mukaiyama reagent (2-chloro-1-methylpyridinium iodide):

The aryl carboxylic acid oligomer (6 mmol, **3**, **8a-g**, **11**), Mukaiyama reagent (6 mmol) and Et_3N (12 mmol) were dissolved in anhydrous dichloromethane (100 mL). The solution was refluxed for 15 min. under N_2. Then a solution of the corresponding arylamine (5 mmol, **2, 4, 7, 14a-c, 17, 19**) in anhydrous dichloromethane (20 mL) was added to the reaction mixture and resulting solution was refluxed for 2 days. The solvent was evaporated under vacuum and the residue was subjected to silica gel column chromatography using the mixture of hexanes/ dichloromethane (2:3) as an eluent to give amide coupling products in the moderate to good yields.

Compound 6: yield 69%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.01 (d, *J* = 6.8 Hz, 6H, Me_{isobut}), 1.39 (s, 9H, Boc), 1.49-1.57 (m, 2H, CH_2), 1.72-1.79 (m, 2H, CH_2), 2.06-2.15 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.96-3.01 (m, 2H, CH_2), 3.89 (s, 3H, COOMe), 3.90 (d, *J* = 6.8 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.24 (t, *J* = 7.5 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 6.87-6.90 (m, 1H, NHBoc), 7.60-8.05 (m, 6H, ArH), 9.84 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6): δ 19.0, 25.8, 25.9, 27.8, 28.2, 52.2, 69.1, 74.5, 77.4, 112.3, 113.9, 119.5, 121.8, 123.4, 125.1, 126.8, 131.2, 139.2, 141.2, 150.4, 150.9, 155.6, 163.6, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{28}H_{37}N_3O_9$ (m/z = 560.2603). Observed m/z = 560.2599. MALDI-TOF, M = $C_{28}H_{37}N_3O_9$ ($[M-H]^+$, m/z = 558.83).

Note: if oxalyl chloride was used to generate an acyl chloride for the coupling reaction between **3** and **4** (DIPEA as a base), the complex mixture of products was obtained from which diamide **5** could be separated.

Compound 5: ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.16 (d, *J* = 6.9 Hz, 12H, Me_{isobut}), 2.16-2.23

(m, 2H, OCH_2CHMe_2), 3.92 (s, 6H, COOMe), 4.05 (d, *J* = 6.1 Hz, 4H, OCH_2CHMe_2), 7.66-8.44 (m, 6H, ArH), 10.16 (s, 2H, NHCO). FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{26}H_{32}N_2O_8$ (m/z = 501.2231). Observed m/z = 501.2236. MALDI-TOF, M = $C_{26}H_{32}N_2O_8$ ($[M]^+$, m/z = 500.32).

Compound 9a: yield 43%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 1.05 (d, *J* = 6.6 Hz, 6H, Me_{isobut}), 1.34 (s, 9H, Boc), 1.37-1.38 (m, 6H, $Me_{isoprop}$), 1.64-1.67 (m, 2H, CH_2), 1.83-1.88 (m, 2H, CH_2), 2.12-2.20 (m, 1H, OCH_2CHMe_2), 3.15-3.17 (m, 2H, CH_2), 3.85 (s, 3H, COOMe), 3.87 (d, *J* = 6.3 Hz, 2H, OCH_2CHMe_2), 4.14 (t, *J* = 6.1 Hz, 2H, $OCH_2(CH_2)_3$), 4.56 (s, 1H, NHBoc), 4.72-4.78 (m, 1H, $OCHMe_2$), 7.31-8.58 (m, 9H, ArH), 8.71 (s, 1H, NHCO), 8.79 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.4, 20.8, 25.3, 25.9, 27.3, 39.3, 51.1, 67.6, 72.1, 74.1, 78.4, 109.5, 110.5, 114.6, 116.2, 117.3, 117.8, 118.2, 122.4, 124.1, 124.9, 129.6, 129.7, 131.1, 138.3, 141.9, 145.9, 146.7, 150.5, 154.9, 162.4, 163.2, 165.7. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{38}H_{48}N_4O_{11}$ (m/z = 737.3392). Observed m/z = 737.3380. MALDI-TOF, M = $C_{38}H_{48}N_4O_{11}$ ($[M-H]^+$, m/z = 735.91).

Compound 9b: yield 89%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 0.99 (d, *J* = 7.0 Hz, 6H, Me_{isobut}), 1.05 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.34 (s, 9H, Boc), 1.62-1.69 (m, 2H, CH_2), 1.83-1.90 (m, 2H, CH_2), 2.07-2.21 (m, 2H, OCH_2CHMe_2), 3.14-3.19 (m, 2H, CH_2), 3.85 (s, 3H, COOMe), 3.87-3.91 (m, 4H, OCH_2CHMe_2), 4.14 (t, *J* = 7.0 Hz, 2H, $OCH_2(CH_2)_3$), 4.58 (s, 1H, NHBoc), 7.32-8.57 (m, 9H, ArH), 8.72 (s, 1H, NHCO), 8.78 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.0, 18.3, 25.3, 26.0, 27.2, 27.3, 39.3, 51.4, 67.6, 74.1, 75.0, 78.4, 109.5, 110.5, 113.2, 116.1, 117.3, 117.8, 118.3, 122.3, 124.1, 125.0, 129.5, 129.7, 131.1, 138.5, 140.7, 145.9, 146.7, 151.8, 155.0, 162.4, 163.2, 165.7. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{39}H_{50}N_4O_{11}$ (m/z = 751.3549). Observed m/z = 751.3544. MALDI-TOF, M = $C_{39}H_{50}N_4O_{11}$ ($[M]^+$, m/z = 750.02).

Compound 9c: yield 51%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 1.05 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.33 (s, 9H, Boc), 1.62-1.67 (m, 2H, CH_2), 1.82-1.89 (m, 2H, CH_2), 2.12-2.19 (m, 1H, OCH_2CHMe_2), 3.13-3.18 (m, 2H, CH_2), 3.84 (s, 3H, COOMe), 3.86 (d, *J* = 6.4 Hz, 2H, OCH_2CHMe_2), 4.13 (t, *J* = 6.3 Hz, 2H, $OCH_2(CH_2)_3$), 4.58 (s, 1H, NHBoc), 5.26 (s, 2H, CH_2Ph), 7.27-8.55 (m, 14H, ArH), 8.71 (s, 1H, NHCO), 8.77 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 19.4, 26.4, 27.1, 28.4, 40.3, 52.2, 68.7, 71.4, 75.1, 79.4, 110.5, 111.5, 115.0, 117.8, 118.4, 118.9, 119.3, 123.4, 125.1, 126.2, 127.2, 128.5, 128.8, 130.6, 132.1, 135.0, 139.6, 142.1, 147.0, 147.8, 152.2, 156.0, 163.2, 164.2, 166.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{42}H_{48}N_4O_{11}$ (m/z = 785.3392). Observed m/z = 785.3406. MALDI-TOF, M = $C_{42}H_{48}N_4O_{11}$ ($[M]^+$, m/z = 784.10).

Compound 9d: yield 35%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 0.86 (t, *J* = 8.2 Hz, 6H, CH_3), 1.05 (d, *J* = 6.8 Hz, 6H, Me_{isobut}), 1.34 (s, 9H, Boc), 1.41-1.49 (m, 4H, $CHCH_2Me$), 1.62-1.72 (m, 3H, CH_2+OCH_2CHEt_2), 1.83-1.90 (m, 2H, CH_2), 2.13-2.21 (m, 1H, OCH_2CHMe_2), 3.14-3.19 (m, 2H, CH_2), 3.85 (s, 3H, COOMe), 3.87 (d, *J* = 6.8 Hz, 2H, OCH_2CHMe_2), 4.03 (d, *J* = 6.2 Hz, 2H, OCH_2CHEt_2), 4.15 (t, *J* = 5.6 Hz, 2H, $OCH_2(CH_2)_3$), 4.56 (s, 1H, NHBoc), 7.32-8.58 (m, 9H, ArH), 8.73 (s, 1H, NHCO), 8.79 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 11.1, 19.4, 23.2, 26.4, 27.0, 28.4, 40.3, 40.8, 52.2, 68.7, 71.9, 75.1, 79.5, 110.6, 111.5, 114.3, 117.1, 118.4, 118.9, 119.3, 123.4, 125.1, 126.1, 130.6, 130.7, 132.2, 139.6, 141.8, 147.0, 147.8, 153.0, 156.0, 163.5, 164.3, 166.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{41}H_{54}N_4O_{11}$ (m/z = 779.3862). Observed m/z = 779.3850. MALDI-TOF, M = $C_{41}H_{54}N_4O_{11}$ ($[M]^+$, m/z = 778.84).

Compound 9e: yield 6%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 1.05 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.36 (s, 9H, Boc), 1.45 (d, *J* = 6.2 Hz, 6H, $Me_{isoprop}$), 1.57-1.65 (m, 2H, CH_2), 1.83-1.90 (m, 2H, CH_2), 2.11-2.21 (m, 1H, OCH_2CHMe_2), 3.13-3.14 (m, 2H, CH_2), 3.85 (s, 3H, COOMe), 3.87 (d, *J* = 6.4 Hz, 2H, OCH_2CHMe_2), 4.15 (t, *J* = 7.0 Hz, 2H, $OCH_2(CH_2)_3$), 4.52 (s, 1H,

NHBoc), 5.48-5.58 (m, 1H, OCHMe$_2$), 7.35-8.68 (m, 8H, ArH), 8.79 (s, 1H, NHCO), 10.19 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 19.4, 21.9, 26.5, 28.4, 52.2, 68.6, 71.7, 75.1, 110.8, 111.5, 115.2, 118.4, 118.9, 119.2, 123.4, 125.1, 130.4, 130.6, 132.2, 136.6, 136.7, 147.0, 148.0, 150.3, 154.8, 155.9, 160.2, 164.3, 166.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{37}H_{47}N_5O_{11}$ (m/z = 738.3345). Observed m/z = 738.3356. MALDI-TOF, M = $C_{37}H_{47}N_5O_{11}$ ($[M]^+$, m/z = 737.91).

Compound 9f: yield 79%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.03 (d, *J* = 6.7 Hz, 6H, Me$_{isobut}$), 1.35 (s, 9H, Boc), 1.50-1.60 (m, 2H, CH_2), 1.76-1.83 (m, 2H, CH_2), 2.09-2.19 (m, 1H, OCH$_2$CHMe$_2$), 2.97-3.02 (m, 2H, CH_2), 3.88 (s, 3H, COOMe), 3.93 (d, *J* = 6.1 Hz, 2H, OCH$_2$CHMe$_2$), 4.14 (t, *J* = 6.1 Hz, 2H, OCH$_2$(CH$_2$)$_3$), 4.82 (s, 2H, OCH$_2$CONH$_2$), 6.85-6.88 (m, 1H, NHBoc), 7.46-8.15 (m, 11H, ArH+CONH$_2$), 9.51 (s, 1H, NHCO), 9.86 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 19.0, 25.9, 26.1, 27.8, 28.2, 52.1, 67.5, 68.3, 74.5, 77.4, 111.1, 112.0, 114.6, 119.8, 120.0, 122.0, 123.7, 125.6, 125.9, 129.9, 131.6, 131.8, 139.3, 140.9, 149.6, 150.4, 150.7, 155.6, 163.4, 164.3, 165.8, 168.6. FT-ICR MS (MeCN): Calculated for $[M-H]^+$, M = $C_{37}H_{45}N_5O_{12}$ (m/z = 750.2992). Observed m/z = 750.2963. MALDI-TOF, M = $C_{37}H_{45}N_5O_{12}$ ($[M-H]^+$, m/z = 750.82).

Compound 9g: yield 88%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.04 (d, *J* = 6.8 Hz, 6H, Me$_{isobut}$), 1.35 (s, 9H, Boc), 1.51-1.60 (m, 2H, CH_2), 1.76-1.83 (m, 2H, CH_2), 2.09-2.19 (m, 1H, OCH$_2$CHMe$_2$), 2.97-3.02 (m, 2H, CH_2), 3.74 (s, 3H, OCH$_2$COOCH$_3$), 3.88 (s, 3H, COOMe), 3.93 (d, *J* = 6.6 Hz, 2H, OCH$_2$CHMe$_2$), 4.14 (t, *J* = 6.1 Hz, 2H, OCH$_2$(CH$_2$)$_3$), 5.17 (s, 2H, OCH$_2$COOMe), 6.84 (s, 1H, NHBoc), 7.60-8.15 (m, 9H, ArH), 9.50 (s, 1H, NHCO), 9.81 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 19.0, 26.0, 27.9, 28.2, 52.0, 54.9, 65.7, 68.4, 74.6, 77.4, 112.1, 114.5, 119.8, 120.6, 122.1, 123.7, 125.2, 125.9, 130.0, 131.6, 131.9, 139.1, 141.6, 149.6, 150.0, 150.4, 155.6, 163.4, 164.3, 165.8, 168.3. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{38}H_{46}N_4O_{13}$ (m/z = 767.3134). Observed m/z = 767.3133. MALDI-TOF, M = $C_{38}H_{46}N_4O_{13}$ ($[M]^+$, m/z = 766.62).

Compound 9h: yield 68%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 1.15 (d, *J* = 6.3 Hz, 6H, Me$_{isobut}$), 1.44 (s, 9H, Boc), 1.47 (s, 9H, Boc), 1.71-1.79 (m, 4H, CH_2), 1.91-2.00 (m, 4H, CH_2), 2.21-2.31 (m, 1H, OCH$_2$CHMe$_2$), 3.22-3.28 (m, 4H, CH_2), 3.95 (s, 3H, COOMe), 3.97 (d, *J* = 7.6 Hz, 2H, OCH$_2$CHMe$_2$), 4.25-4.28 (m, 4H, OCH$_2$(CH$_2$)$_3$), 4.71 (s, 2H, NHBoc), 7.46-8.67 (m, 9H, ArH), 8.82 (s, 1H, NHCO), 8.89 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 19.4, 26.1, 26.4, 26.6, 27.1, 28.4, 40.0, 40.3, 52.2, 68.7, 69.5, 75.1, 79.2, 79.4, 110.6, 111.5, 114.2, 117.6, 118.4, 118.9, 119.3, 123.4, 125.1, 126.2, 130.7, 132.2, 139.7, 141.8, 147.0, 147.8, 152.6,156.0, 163.4, 164.3, 166.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{44}H_{59}N_5O_{13}$ (m/z = 866.4182). Observed m/z = 866.4172. MALDI-TOF, M = $C_{44}H_{59}N_5O_{13}$ ($[M]^+$, m/z = 865.01).

Compound 12: yield 27%; ^{1}H-NMR (500 Hz, $CDCl_3$, δ): 1.00 (d, *J* = 6.9 Hz, 6H, Me$_{isobut}$), 1.04 (d, *J* = 6.5 Hz, 6H, Me$_{isobut}$), 1.36 (s, 9H, Boc), 1.62-1.68 (m, 2H, CH_2), 1.85-1.91 (m, 2H, CH_2), 2.09-2.20 (m, 2H, OCH$_2$CHMe$_2$), 3.15-3.19 (m, 2H, CH_2), 3.85 (s, 3H, COOMe), 3.89-3.93 (m, 4H, OCH$_2$CHMe$_2$), 4.11 (t, *J* = 6.5 Hz, 2H, OCH$_2$(CH$_2$)$_3$), 4.55 (s, 1H, NHBoc), 7.33-8.60 (m, 9H, ArH), 8.71 (s, 2H, NHCO). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 19.0, 19.3, 26.4, 26.8, 28.1, 28.2, 28.4, 40.1, 52.1, 68.4, 75.2, 76.1, 79.3, 110.7, 111.6, 113.7, 117.3, 118.7, 118.8, 118.9, 123.5, 125.2, 125.9, 130.6, 130.7, 132.0, 139.7, 141.7, 146.8, 147.8, 152.8, 155.9, 163.1, 164.4, 166.7. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{39}H_{50}N_4O_{11}$ (m/z = 751.3549). Observed m/z = 751.3550. MALDI-TOF, M = $C_{39}H_{50}N_4O_{11}$ ($[M]^+$, m/z = 750.02).

Compound 15a: yield 47%; ^{1}H-NMR (500 Hz, $CDCl_3$, δ): 1.33-1.40 (m, 21H, Boc+ Me$_{isoprop}$), 1.63-1.68 (m, 2H, CH_2), 1.82-1.87 (m, 2H, CH_2), 3.13-3.17 (m, 2H, CH_2), 3.85 (s, 3H, COOMe), 4.16 (t, *J* = 5.8 Hz, 2H, OCH$_2$(CH$_2$)$_3$), 4.58 (s, 1H, NHBoc), 4.68-4.78 (m, 2H,

OCHMe$_2$), 7.31-8.58 (m, 9H, ArH), 8.71 (s, 1H, NHCO), 8.79 (s, 1H, NHCO). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 22.2, 26.1, 26.6, 28.4, 39.9, 45.7, 52.1, 69.5, 71.8, 71.9, 79.2, 111.8, 113.1, 114.1, 117.4, 118.5, 118.7, 119.2, 123.3, 125.1, 126.0, 130.6, 131.3, 132.9, 139.8, 141.7, 145.7, 146.6, 152.6, 156.0, 163.1, 164.3, 166.7. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{37}H_{46}N_4O_{11}$ (m/z = 723.3236). Observed m/z = 723.3220. MALDI-TOF, M = $C_{37}H_{46}N_4O_{11}$ ($[M]^+$, m/z = 722.58).

Compound 15b: yield 60%; ^{1}H-NMR (500 Hz, $CDCl_3$, δ): 1.03 (d, *J* = 6.5 Hz, 6H, Me$_{isobut}$), 1.05 (d, *J* = 7.1 Hz, 6H, Me$_{isobut}$), 1.37 (s, 9H, Boc), 1.62-1.68 (m, 2H, CH$_2$), 1.82-1.87 (m, 2H, CH$_2$), 2.11-2.20 (m, 2H, OCH$_2$CHMe$_2$), 3.13-3.17 (m, 2H, CH$_2$), 3.85 (s, 3H, COOMe), 3.87 (d, *J* = 6.1 Hz, 2H, OCH$_2$CHMe$_2$), 3.90 (d, *J* = 6.9 Hz, 2H, OCH$_2$CHMe$_2$), 4.15 (t, *J* = 5.8 Hz, 2H, OCH$_2$(CH$_2$)$_3$), 4.57 (s, 1H, NHBoc), 7.34-8.59 (m, 9H, ArH), 8.71 (s, 1H, NHCO), 8.79 (s, 1H, NHCO). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 19.3, 19.4, 26.1, 26.6, 28.2, 28.3, 28.4, 40.0, 52.1, 69.5, 75.1, 75.2, 79.2, 110.4, 111.5, 113.9, 117.4, 118.3, 119.0, 123.4, 125.1, 126.0, 130.6, 130.7, 132.1, 139.8, 141.7, 147.0, 147.8, 152.6, 156.0, 163.0, 164.3, 166.7. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{39}H_{50}N_4O_{11}$ (m/z = 751.3549). Observed m/z = 751.3551. MALDI-TOF, M = $C_{39}H_{50}N_4O_{11}$ ($[M]^+$, m/z = 750.71).

Compound 15c: yield 51%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 0.90-0.95 (m, 12H, CH$_3$), 1.37 (s, 9H, Boc), 1.43-1.52 (m, 8H, CHCH$_2$Me), 1.60-1.74 (m, 4H, CH$_2$+OCH$_2$CHEt$_2$), 1.81-1.88 (m, 2H, CH$_2$), 3.14-3.15 (m, 2H, CH$_2$), 3.85 (s, 3H, COOMe), 4.01 (d, *J* = 5.3 Hz, 2H, OCH$_2$CHEt$_2$), 4.04 (d, *J* = 5.4 Hz, 2H, OCH$_2$CHEt$_2$), 4.14 (t, *J* = 5.9 Hz, 2H, OCH$_2$(CH$_2$)$_3$), 4.58 (s, 1H, NHBoc), 7.31-8.59 (m, 9H, ArH), 8.71 (s, 1H, NHCO), 8.77 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 11.3, 11.4, 23.8, 23.9, 26.2, 26.7, 28.4, 40.0, 41.0, 41.1, 52.2, 69.5, 70.7, 71.0, 79.2, 110.5, 111.5, 114.1, 117.3, 118.4, 118.9, 123.4, 125.1, 126.0, 130.6, 130.8, 132.2, 139.8, 141.7, 147.1, 148.0, 152.7, 156.1, 163.1, 164.3, 166.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{43}H_{58}N_4O_{11}$ (m/z = 807.4175). Observed m/z = 807.4172. MALDI-TOF, M = $C_{43}H_{58}N_4O_{11}$ ($[M]^+$, m/z = 806.15).

Compound 18: yield 76%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.35 (d, *J* = 6.0 Hz, 6H, Me$_{isoprop}$), 1.39 (s, 9H, Boc), 1.51-1.58 (m, 2H, CH$_2$), 1.72-1.79 (m, 2H, CH$_2$), 2.97-3.02 (m, 2H, CH$_2$), 3.88 (s, 3H, COOMe), 4.27 (t, *J* = 6.4 Hz, 2H, OCH$_2$(CH$_2$)$_3$), 4.72-4.78 (m, 1H, OCHMe$_2$), 6.88-6.91 (m, 1H, NHBoc), 7.61-8.11 (m, 6H, ArH), 9.74 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6): δ 21.6, 25.8, 25.9, 28.2, 52.2, 69.1, 71.4, 77.4, 113.9, 114.1, 119.5, 121.9, 122.9, 125.1, 126.4, 132.2, 139.3, 141.2, 148.6, 150.9, 155.6, 163.7, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{27}H_{35}N_3O_9$ (m/z = 546.2446). Observed m/z = 546.2438. MALDI-TOF, M = $C_{27}H_{35}N_3O_9$ ($[M-H]^+$, m/z = 544.91).

Compound 20: yield 47%; ^{1}H-NMR (400 Hz, $CDCl_3$, δ): 1.0 (d, *J* = 6.7 Hz, 6H, Me$_{isobut}$), 1.34 (s, 9H, Boc), 1.38 (d, *J* = 6.0 Hz, 6H, Me$_{isoprop}$), 1.64-1.67 (m, 2H, CH$_2$), 1.83-1.90 (m, 2H, CH$_2$), 2.07-2.17 (m, 1H, OCH$_2$CHMe$_2$), 3.14-3.18 (m, 2H, CH$_2$), 3.84 (s, 3H, COOMe), 3.90 (d, *J* = 6.4 Hz, 2H, OCH$_2$CHMe$_2$), 4.15 (t, *J* = 6.4 Hz, 2H, OCH$_2$(CH$_2$)$_3$), 4.56 (s, 1H, NHBoc), 4.69-4.72 (m, 1H, OCHMe$_2$), 7.33-8.57 (m, 9H, ArH), 8.72 (s, 1H, NHCO), 8.80 (s, 1H, NHCO). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 18.0, 21.2, 25.3, 26.0, 27.2, 27.3, 51.1, 67.6, 70.8, 75.0, 78.4, 109.6, 112.1, 113.2, 116.2, 117.6, 117.9, 118.3, 122.3, 124.1, 125.0, 129.6, 131.9, 138.6, 140.7, 144.8, 146.7, 151.8, 155.0, 162.4, 163.3, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{38}H_{48}N_4O_{11}$ (m/z = 737.3392). Observed m/z = 737.3388. MALDI-TOF, M = $C_{38}H_{48}N_4O_{11}$ ($[M]^+$, m/z = 736.49).

General protocol for Boc-deprotection of oligomers:

The corresponding Boc-protected oligomer (0.1 mmol, **9a-h**, **12**, **15a-c**, **20**) was dissolved in chloroform (1 mL), then 0.5 mL of trifluoroacetic acid (TFA) was added and the reaction mixture was stirred for 3-5 hr. Solvent was evaporated under reduced pressure to the

dryness and the residue was sonicated with a small volume of acetonitrile. Suspension formed was filtered off to give a yellow solid of NH_2-oligomer in the nearly quantitative yield.

Compound 10a: yield 97%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.08 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.40 (d, *J* = 6.0 Hz, 6H, $Me_{isoprop}$), 1.75-1.80 (m, 2H, CH_2), 1.89-1.94 (m, 2H, CH_2), 2.14-2.24 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.89-2.91 (m, 2H, CH_2), 3.92 (s, 3H, COOMe), 3.98 (d, *J* = 6.3 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.21 (t, *J* = 6.3 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 4.99-5.05 (m, 1H, $OC\underline{H}Me_2$), 7.64-8.18 (m, 12H, ArH+NH_3), 9.56 (s, 1H, NHCO), 9.91 (s, 1H, NHCO). ^{13}C NMR (125 MHz, DMSO-d6, δ): 19.0, 21.5, 23.6, 25.5, 27.8, 38.4, 52.0, 67.8, 72.4, 74.5, 111.3, 112.1, 115.2, 119.6, 119.7, 122.0, 122.1, 123.8, 124.9, 126.0, 129.9, 131.6, 131.8, 139.0, 142.4, 149.6, 149.7, 150.4, 163.6, 164.3, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{33}H_{40}N_4O_9$ (m/z = 637.2868). Observed m/z = 637.2831. MALDI-TOF, M = $C_{33}H_{40}N_4O_9$ ($[M+2H]^{2+}$, m/z = 638.37).

Compound 10b: yield 82%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.11 (dd, J_1 = 6.6 Hz, J_2 = 6.9 Hz, 12H, Me_{isobut}), 1.78-1.85 (m, 2H, CH_2), 1.94-2.01 (m, 2H, CH_2), 2.15-2.27 (m, 2H, $OCH_2C\underline{H}Me_2$), 2.94 (t, *J* = 7.4 Hz, 2H, CH_2), 3.98 (s, 3H, COOMe), 4.03 (d, *J* = 6.6 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.15 (d, *J* = 6.2 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.26 (t, *J* = 6.9 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 7.70-8.24 (m, 12H, ArH+NH_3), 9.61 (s, 1H, NHCO), 9.97 (br s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 18.8, 19.0, 23.7, 25.5, 27.6, 27.8, 38.5, 52.2, 67.7, 74.5, 75.2, 111.4, 112.1, 114.0, 115.8, 118.8, 119.5, 119.7, 122.2, 124.0, 125.1, 126.0, 129.9, 131.7, 131.8, 139.3, 141.2, 149.7, 150.6, 151.1, 157.8, 158.1, 163.6, 164.3, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{34}H_{42}N_4O_9$ (m/z = 651.3025). Observed m/z = 651.3015. MALDI-TOF, M = $C_{34}H_{42}N_4O_9$ ($[M+2H]^{2+}$, m/z = 652.56).

Compound 10c: yield 39%; ^{1}H-NMR (500 Hz, DMSO-d6, δ): 1.05 (d, *J* = 7.0 Hz, 6H, Me_{isobut}), 1.70-1.76 (m, 2H, CH_2), 1.87-1.90 (m, 2H, CH_2), 2.13-2.19 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.87 (br s, 2H, CH_2), 3.89 (s, 3H, COOMe), 3.95 (d, *J* = 6.8 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.18 (t, *J* = 6.8 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 5.45 (s, 2H, $C\underline{H}_2Ph$), 7.39-8.15 (m, 17H, ArH+NH_3), 9.52 (s, 1H, NHCO), 9.90 (s, 1H, NHCO). ^{13}C NMR (125 MHz, DMSO-d6, δ): 19.4, 24.1, 26.0, 28.2, 52.6, 68.3, 71.3, 75.0, 111.9, 112.6, 115.2, 120.4, 122.6, 124.4, 125.7, 126.5, 127.9, 128.7, 129.0, 130.4, 132.2, 136.2, 139.7, 141.9, 150.1, 151.0,151.2, 164.0, 164.8, 166.2. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{37}H_{40}N_4O_9$ (m/z = 685.2868). Observed m/z = 685.2846. MALDI-TOF, M = $C_{37}H_{40}N_4O_9$ ($[M+2H]^{2+}$, m/z = 686.83).

Compound 10d: yield 96%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 0.91 (t, *J* = 7.4 Hz, 6H, CH_3), 1.04 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.43-1.48 (m, 4H, $CHC\underline{H}_2Me$), 1.69-1.75 (m, 3H, CH_2+$OCH_2C\underline{H}Et_2$), 1.86-1.90 (m, 2H, CH_2), 2.09-2.18 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.85 (t, *J* = 7.5 Hz, 2H, CH_2), 3.88 (s, 3H, COOMe), 3.93 (d, *J* = 6.3 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.18-4.19 (m, 4H, $OC\underline{H}_2CHEt_2$+$OC\underline{H}_2(CH_2)_3$), 7.60-8.14 (m, 12H, ArH+NH_3), 9.51 (s, 1H, NHCO), 9.89 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 10.9, 19.0, 22.7, 23.6, 25.5, 27.8, 52.1, 67.7, 71.3, 74.5, 111.3, 112.1, 114.1, 119.5, 119.7, 122.0, 122.1, 123.9, 125.0, 126.0, 129.9, 131.7, 131.8, 139.3, 141.2, 149.6, 150.5, 151.2, 163.7, 164.3, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{36}H_{46}N_4O_9$ (m/z = 679.3338). Observed m/z = 679.3298. MALDI-TOF, M = $C_{36}H_{46}N_4O_9$ ($[M]^+$, m/z = 678.02).

Compound 10e: yield 84%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.05 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.48 (d, *J* = 6.2, 6H, $Me_{isoprop}$), 1.70-1.78 (m, 2H, CH_2), 1.88-1.95 (m, 2H, CH_2), 2.12-2.18 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.86-2.91 (m, 2H, CH_2), 3.87 (s, 3H, COOMe), 3.93 (d, *J* = 6.4 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.28 (t, *J* = 6.7 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 5.55-5.63 (m, 1H, $OC\underline{H}Me_2$), 7.57-8.68 (m, 11H, ArH+NH_3), 9.43 (s, 1H, NHCO), 10.26 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 17.9, 20.4, 22.2, 24.4, 26.7, 37.3, 51.0, 66.8, 70.3, 73.4, 109.6, 110.9, 114.3, 117.3, 119.2, 120.7, 120.9, 124.7, 128.6, 128.9, 130.6, 135.4, 136.3, 146.1, 148.1, 148.3, 152.5, 158.6, 162.9, 164.6. FT-ICR MS (MeCN): Calculated for $[M+H]^+$,

M = $C_{32}H_{39}N_5O_9$ (m/z = 638.2821). Observed m/z = 638.2797. MALDI-TOF, M = $C_{32}H_{39}N_5O_9$ ($[M+2H]^{2+}$, m/z = 639.67).

Compound 10f: yield 99%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.04 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.69-1.77 (m, 2H, CH_2), 1.86-1.92 (m, 2H, CH_2), 2.09-2.19 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.87-2.92 (m, 2H, CH_2), 3.87 (s, 3H, COOMe), 3.93 (d, *J* = 6.6 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.16 (t, *J* = 6.1 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 4.84 (s, 2H, $OC\underline{H}_2CONH_2$), 7.52-8.14 (m, 14H, $ArH+CONH_2+NH_3$), 9.52 (s, 1H, NHCO), 9.90 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 19.0, 23.8, 25.5, 27.8, 38.5, 52.1, 67.5, 67.9, 74.5, 111.3, 112.1, 114.6, 115.7, 118.7, 119.8, 120.2, 122.0, 122.2, 123.9, 125.6, 126.0, 129.8, 131.7, 131.8, 139.2, 140.9, 149.7, 150.5, 150.6, 157.9, 163.4, 164.3, 165.8, 168.8. FT-ICR MS (MeCN): Calculated for $[M-H]^-$, M = $C_{32}H_{37}N_5O_{10}$ (m/z = 650.2468). Observed m/z = 650.2447. MALDI-TOF, M = $C_{32}H_{37}N_5O_{10}$ ($[M]^+$, m/z = 651.20).

Compound 10g: yield 85%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 0.94 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.58-1.66 (m, 2H, CH_2), 1.74-1.81 (m, 2H, CH_2), 2.01-2.09 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.74-2.82 (m, 2H, CH_2), 3.65 (s, 3H, $OCH_2COOC\underline{H}_3$), 3.78 (s, 3H, COOMe), 3.83 (d, *J* = 6.8 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.06 (t, *J* = 6.8 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 5.08 (s, 2H, $OC\underline{H}_2COOMe$), 7.49-8.04 (m, 12H, $ArH+NH_3$), 9.42 (s, 1H, NHCO), 9.76 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 19.0, 23.7, 25.5, 27.8, 38.5, 52.1, 65.7, 67.8, 74.5, 111.3, 112.1, 114.4, 114.9, 119.7, 120.6, 122.0, 122.2, 124.0, 125.2, 126.0, 129.8, 131.7, 131.8, 139.0, 141.6, 149.7, 150.0, 150.5, 158.0, 158.3, 163.4, 164.3, 165.8, 168.3. FT-ICR MS (MeCN): Calculated for $[M-H]^-$, M = $C_{33}H_{38}N_4O_{11}$ (m/z = 665.2453). Observed m/z = 665.2465. MALDI-TOF, M = $C_{33}H_{38}N_4O_{11}$ ($[M]^+$, m/z = 666.21).

Compound 10h: yield 96%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.04 (d, *J* = 6.5 Hz, 6H, Me_{isobut}), 1.72-1.75 (m, 4H, CH_2), 1.85-1.87 (m, 4H, CH_2), 2.11-2.17 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.86-2.92 (m, 4H, CH_2), 3.88 (s, 3H, COOMe), 3.94 (d, *J* = 6.4 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.17 (t, *J* = 5.9 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 4.30 (t, *J* = 7.0 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 7.60-8.14 (m, 15H, $ArH+NH_3$), 9.52 (s, 1H, NHCO), 9.89 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 18.8, 19.0, 23.7, 23.8, 25.4, 25.5, 27.8, 38.5, 52.2, 67.8, 68.9, 74.5, 111.3, 112.1, 114.2, 115.2, 118.2, 119.6, 122.0, 122.2, 124.0, 125.1, 126.0, 129.9, 131.7, 131.8, 139.3, 141.1, 149.7, 150.5, 150.9, 157.7, 158.1, 158.4, 158.7, 163.6, 164.3, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{34}H_{43}N_5O_9$ (m/z = 666.3134). Observed m/z = 666.3124. MALDI-TOF, M = $C_{34}H_{43}N_5O_9$ ($[M+H]^+$, m/z = 666.38).

Compound 13: yield 98%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 0.91-0.95 (m, 12H, Me_{isobut}), 1.61-1.69 (m, 2H, CH_2), 1.77-1.84 (m, 2H, CH_2), 1.95-2.08 (m, 2H, $OCH_2C\underline{H}Me_2$), 2.75-2.81 (m, 2H, CH_2), 3.78 (s, 3H, COOMe), 3.84 (d, *J* = 6.4 Hz, 2H, $OC\underline{H}_2CHMe_2$), 3.95 (d, *J* = 6.5 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.08 (t, *J* = 6.4 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 7.53-8.03 (m, 12H, $ArH+NH_3$), 9.45 (s, 1H, NHCO), 9.80 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 18.7, 19.1, 23.5, 25.4, 27.6, 27.8, 52.1, 67.7, 74.5, 75.2, 111.4, 112.3, 113.8, 114.6, 119.6, 119.7, 122.1, 122.4, 124.0, 125.1, 126.0, 129.9, 131.7, 131.8, 139.3, 141.2, 149.5, 150.9, 151.0, 157.6, 158.0, 158.3, 163.6, 164.4, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{34}H_{42}N_4O_9$ (m/z = 651.3025). Observed m/z = 651.3027. MALDI-TOF, M = $C_{34}H_{42}N_4O_9$ ($[M+H]^+$, m/z = 651.05).

Compound 16a: yield 50%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.37-1.40 (m, 12H, $Me_{isoprop}$), 1.70-1.77 (m, 2H, CH_2), 1.83-1.90 (m, 2H, CH_2), 2.89 (t, *J* = 7.3 Hz, 2H, CH_2), 3.88 (s, 3H, COOMe), 4.32 (t, *J* = 5.7 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 4.75-4.84 (m, 2H, $OC\underline{H}Me_2$), 7.60-8.24 (m, 12H, $ArH+NH_3$), 9.43 (s, 1H, NHCO), 9.78 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 21.7, 21.8, 23.8, 25.4, 52.2, 68.9, 71.3, 71.4, 112.7, 113.7, 114.2, 119.5, 119.8, 121.7, 122.1, 123.6, 125.2, 125.6, 130.9, 131.5, 132.8, 139.4, 141.2, 147.8, 149.2, 150.9, 163.6, 164.3, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{32}H_{38}N_4O_9$ (m/z =

623.2712). Observed m/z = 623.2713. MALDI-TOF, M = $C_{32}H_{38}N_4O_9$ ($[M+2H]^{2+}$, m/z = 624.46).

Compound 16b: yield 79%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.02 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.05 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.70-1.77 (m, 2H, CH_2), 1.83-1.89 (m, 2H, CH_2), 2.08-2.20 (m, 2H, $OCH_2C\underline{H}Me_2$), 2.87-2.93 (m, 2H, CH_2), 3.89 (s, 3H, COOMe), 3.93 (dd, J_1 = 6.5 Hz, J_2= 6.3 Hz, 4H, $OC\underline{H}_2CHMe_2$), 4.30 (t, *J* = 6.1 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 7.60-8.16 (m, 12H, $ArH+NH_3$), 9.53 (s, 1H, NHCO), 9.90 (s, 1H, NHCO). ^{13}C NMR (100 Hz, DMSO-d6, δ): 19.1, 23.8, 25.4, 27.8, 52.2, 68.9, 74.5, 111.1, 112.0, 114.0, 119.6, 119.9, 122.1, 124.1, 125.2, 125.9, 129.9, 131.8, 139.4, 141.1, 141.7, 149.6, 150.9, 157.7, 158.0, 163.6, 164.3, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{34}H_{42}N_4O_9$ (m/z = 651.3025). Observed m/z = 651.3022. MALDI-TOF, M = $C_{34}H_{42}N_4O_9$ ($[M+2H]^{2+}$, m/z = 652.42).

Compound 16c: yield 98%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 0.89-0.94 (m, 12H, CH_3), 1.38-1.57 (m, 8H, $CHC\underline{H}_2Me$), 1.70-1.77 (m, 4H, CH_2+$OCH_2C\underline{H}Et_2$), 1.83-1.89 (m, 2H, CH_2), 2.88-2.93 (m, 2H, CH_2), 3.89 (s, 3H, COOMe), 4.06-4.08 (m, 4H, $OC\underline{H}_2CHEt_2$), 4.29 (t, *J* = 6.0 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 7.60-8.16 (m, 12H, $ArH+NH_3$), 9.49 (s, 1H, NHCO), 9.86 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 11.0, 11.1, 22.9, 23.0, 23.9, 25.4, 52.2, 68.9, 70.3, 111.0, 112.1, 114.0, 114.7, 119.5, 119.9, 122.0, 122.2, 124.2, 125.2, 126.0, 129.9, 131.8, 131.9, 139.4, 141.1, 149.8, 150.9, 151.1, 157.9, 158.3, 163.5, 164.3, 165.9. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{38}H_{50}N_4O_9$ (m/z = 707.3651). Observed m/z = 707.3617. MALDI-TOF, M = $C_{38}H_{50}N_4O_9$ ($[M+2H]^{2+}$, m/z = 708.57).

Compound 21: yield 49%; ^{1}H-NMR (400 Hz, DMSO-d6, δ): 1.06 (d, *J* = 6.7 Hz, 6H, Me_{isobut}), 1.42 (d, *J* = 6.0 Hz, 6H, $Me_{isoprop}$), 1.73-1.81 (m, 2H, CH_2), 1.89-1.96 (m, 2H, CH_2), 2.09-2.19 (m, 1H, $OCH_2C\underline{H}Me_2$), 2.91 (br s, 2H, CH_2), 3.92 (s, 3H, COOMe), 4.11 (d, *J* = 6.4 Hz, 2H, $OC\underline{H}_2CHMe_2$), 4.23 (t, *J* = 6.4 Hz, 2H, $OC\underline{H}_2(CH_2)_3$), 4.78-4.87 (m, 1H, $OC\underline{H}Me_2$), 7.66-8.26 (m, 12H, $ArH+NH_3$), 9.48 (s, 1H, NHCO), 9.94 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO-d6, δ): 18.8, 21.7, 23.6, 25.5, 27.7, 52.2, 67.7, 71.5, 75.3, 111.5, 113.8, 114.1, 119.5, 119.6, 121.7, 122.1, 124.1, 125.1, 125.7, 130.0, 131.7, 132.7, 139.3, 141.2, 147.9, 150.6, 151.1, 163.6, 164.3, 165.8. FT-ICR MS (MeCN): Calculated for $[M+H]^+$, M = $C_{33}H_{40}N_4O_9$ (m/z = 637.2868). Observed m/z = 637.2831. MALDI-TOF, M = $C_{33}H_{40}N_4O_9$ ($[M+H]^+$, m/z = 637.86).

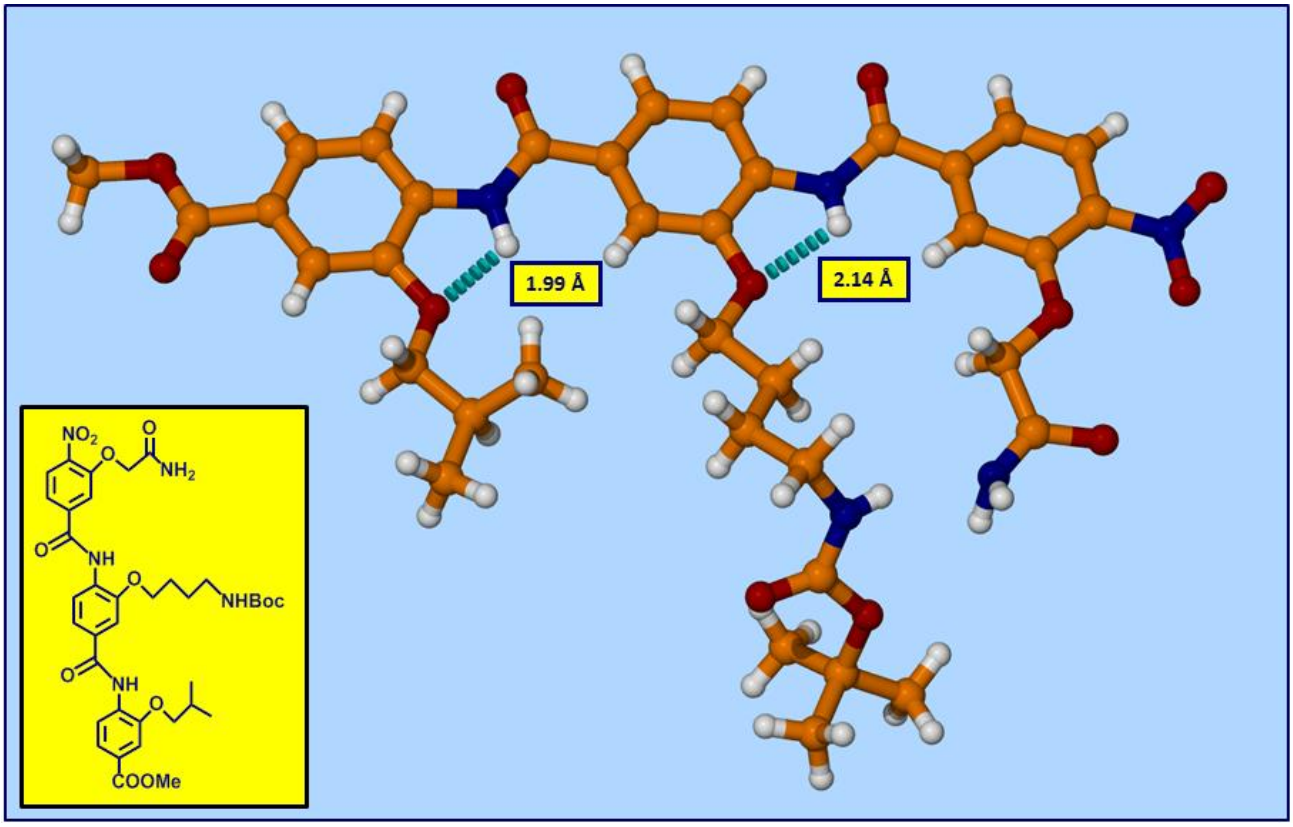

Figure S1. Molecular structure of trimer **9f**

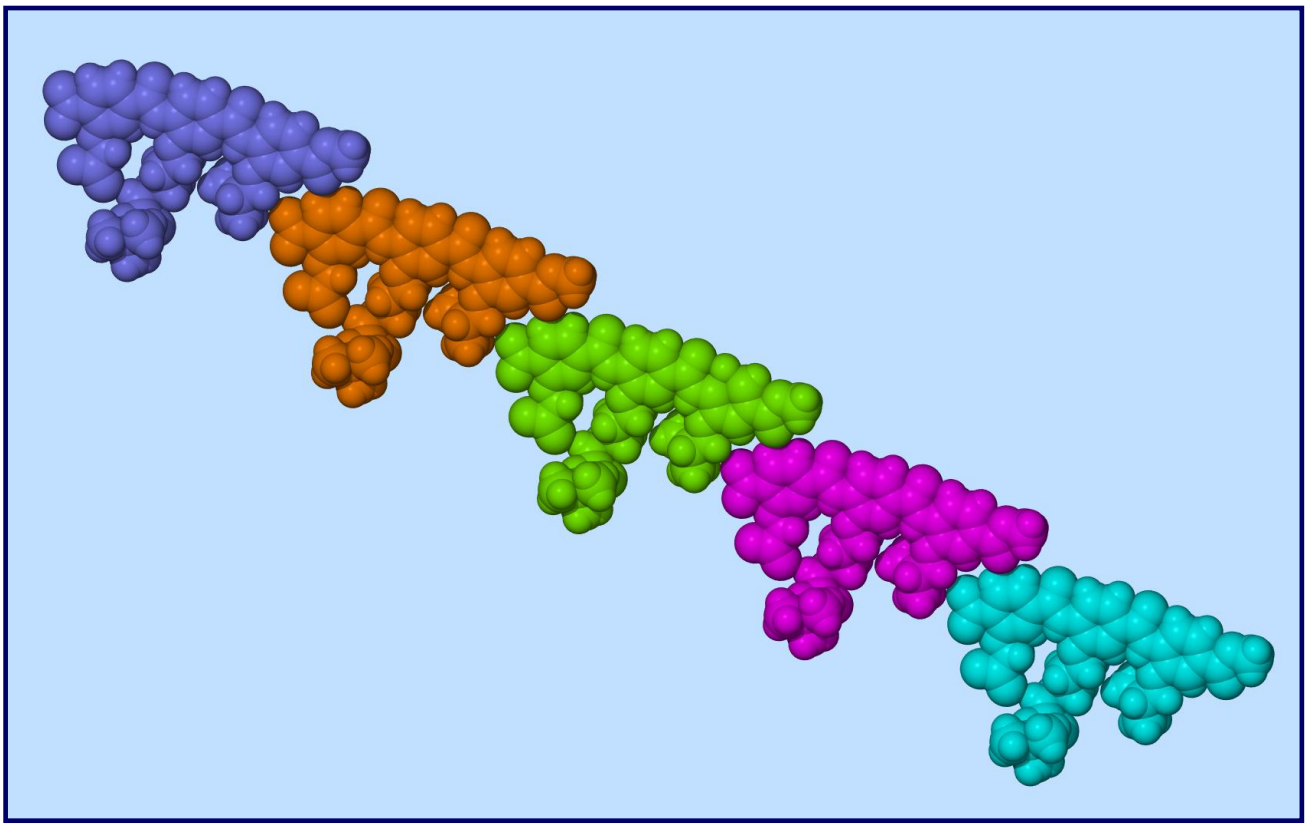

Figure S2. Partial crystal packing diagram of **9f** in CPK format (disordered $CHCl_3$ molecules omitted for clarity)

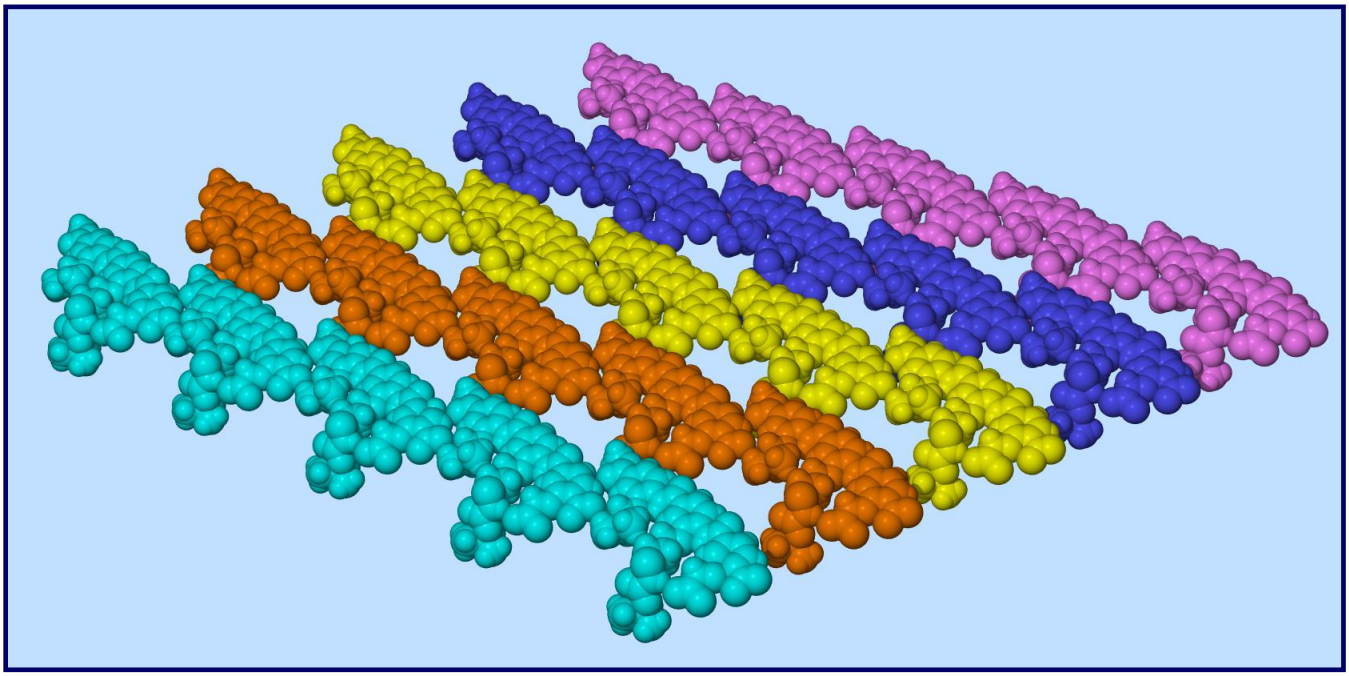

Figure S3. Partial crystal packing diagram of **9f** showcasing the formation of molecular layer (disordered $CHCl_3$ molecules filling the voids in the assembly not shown)

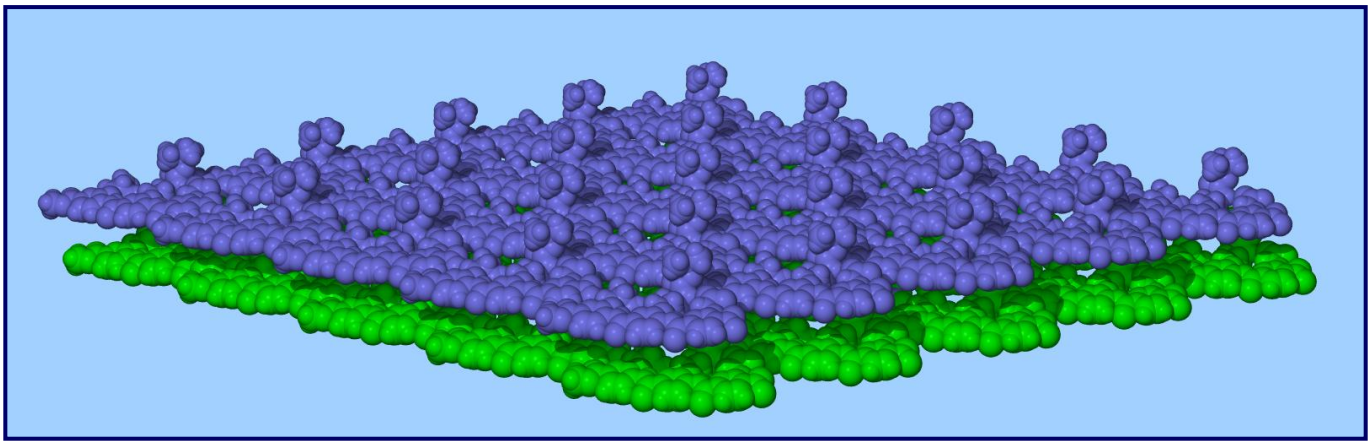

Figure S4. Partial crystal packing diagram of **9f**: two layers (each in its own color)

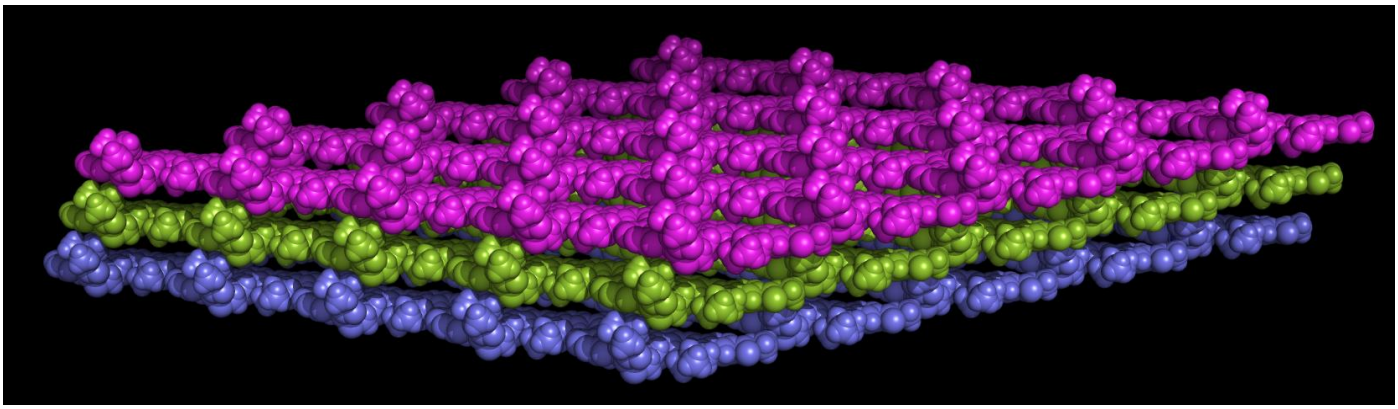

Figure S5. Partial crystal packing diagram of **9f**: three layers (each in its own color)

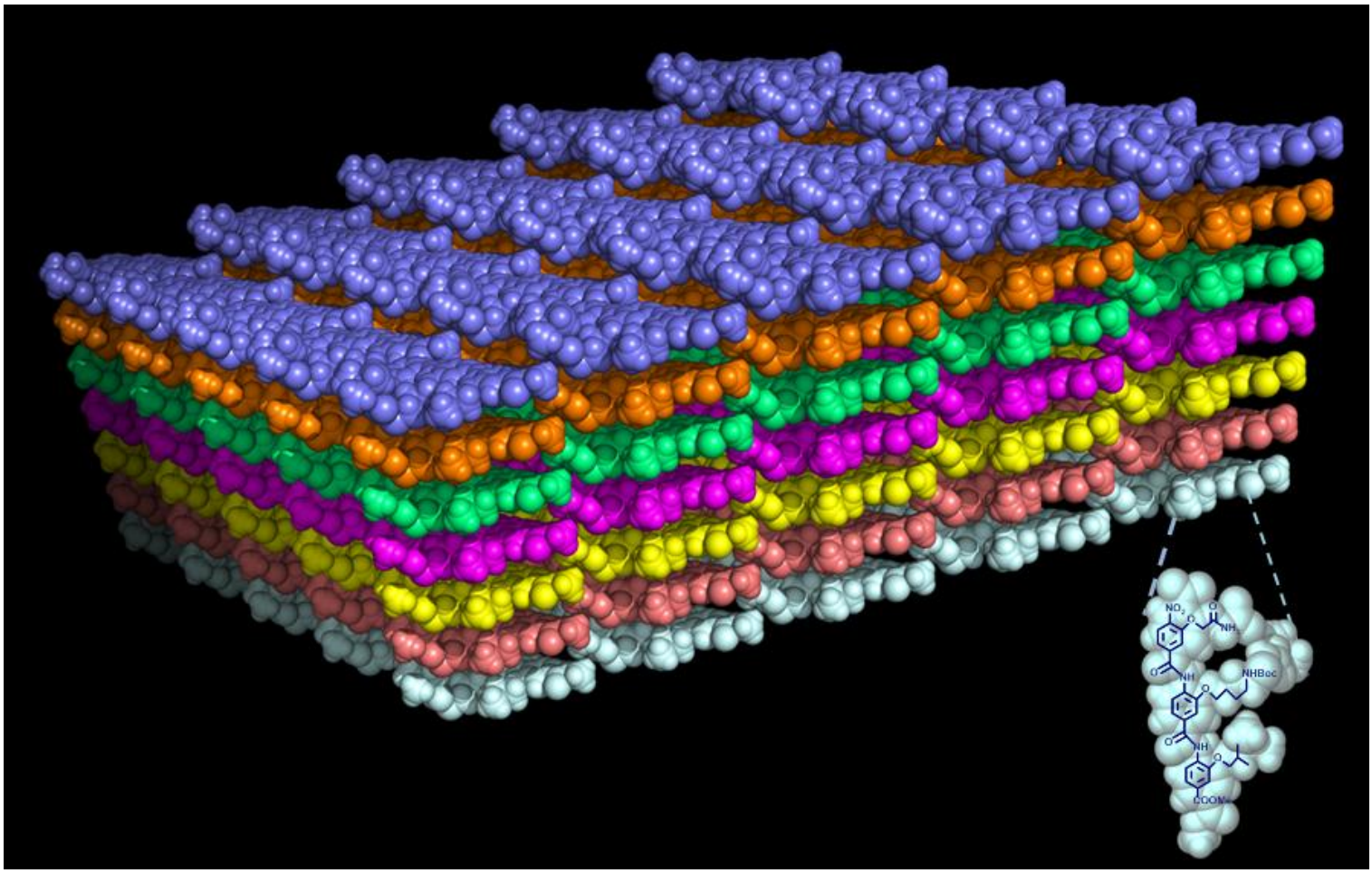

Figure S6. Partial crystal packing diagram of **9f**: an array of 5x5x7 of individual molecules shown (each layer in its own color)

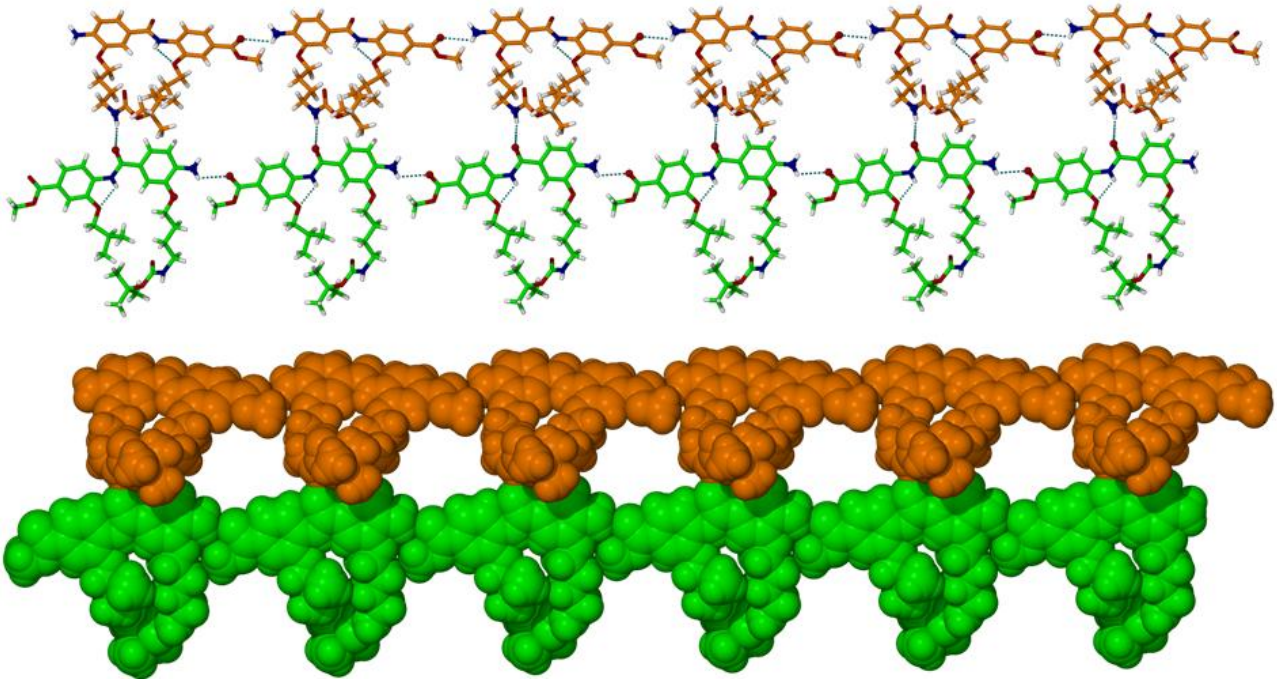

Figure S7. Partial crystal packing diagram of dimer **7**, pattern 1 (CPK and ball-and-stick format)

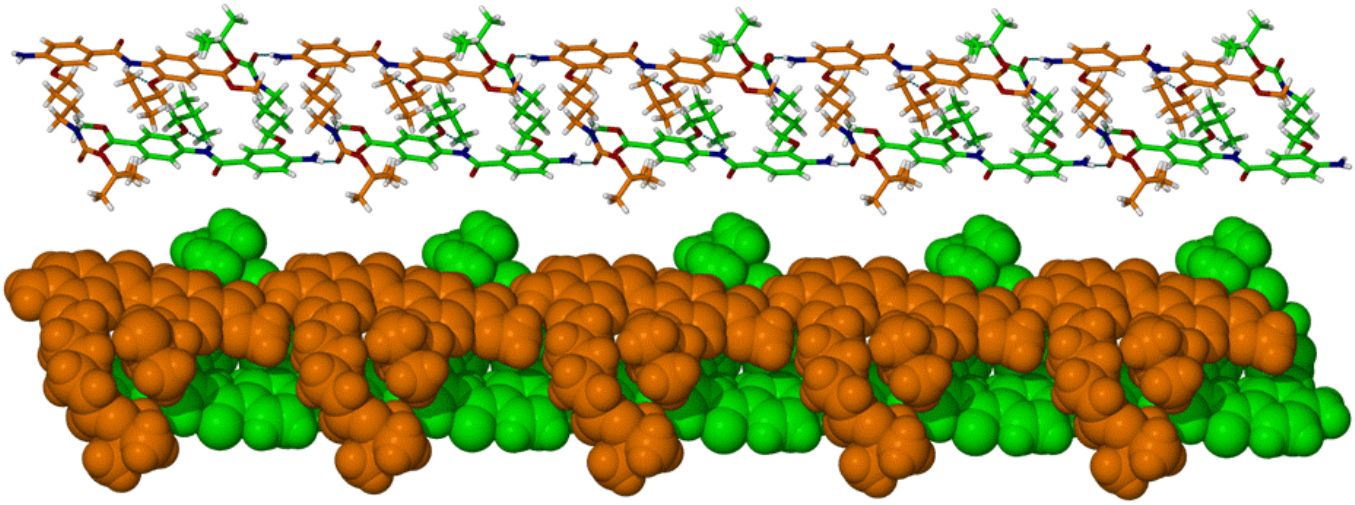

Figure S8. Partial crystal packing diagram of dimer **7**, pattern 2 (CPK and ball-and-stick format)

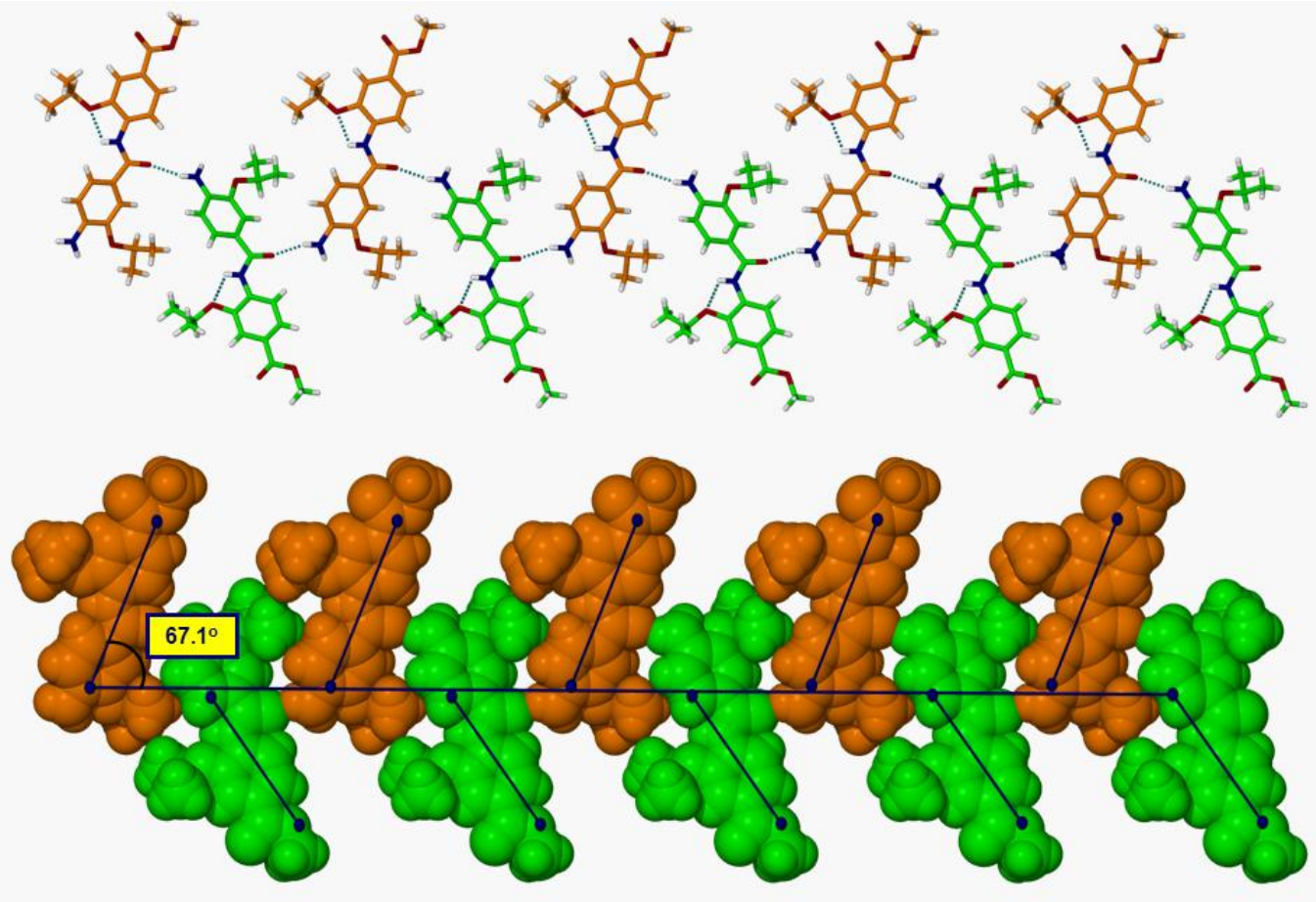

Figure S9. Partial crystal packing diagram of dimer **14a**: formation of the infinite supramolecular chains through the hydrogen bonding between NH_2- and O=C-NH groups (CPK and ball-and-stick format)

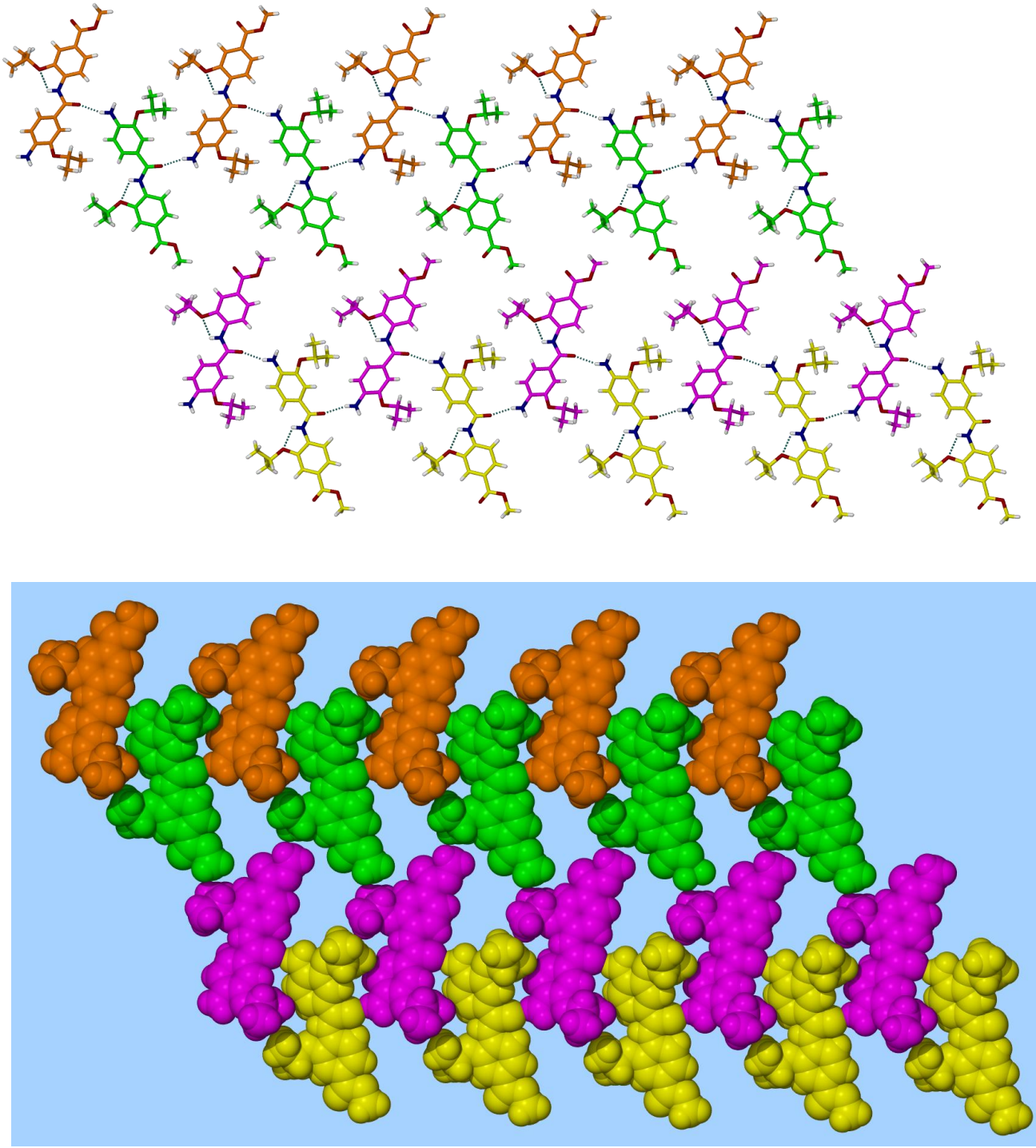

Figure S10. Partial crystal packing diagram of dimer **14a**: communication of individual chains in the crystal lattice (CPK and ball-and-stick format)

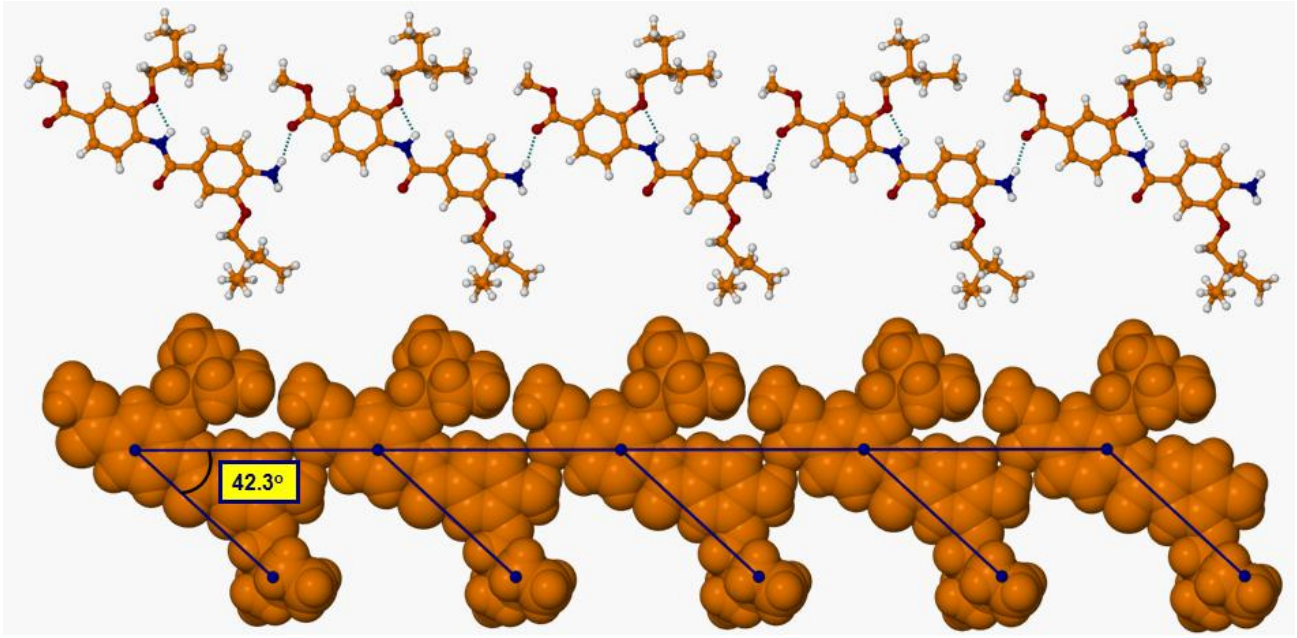

Figure S11. Packing motif of dimer **14c**: formation of the infinite linear H-bonded network (CPK and ball-and-stick format)

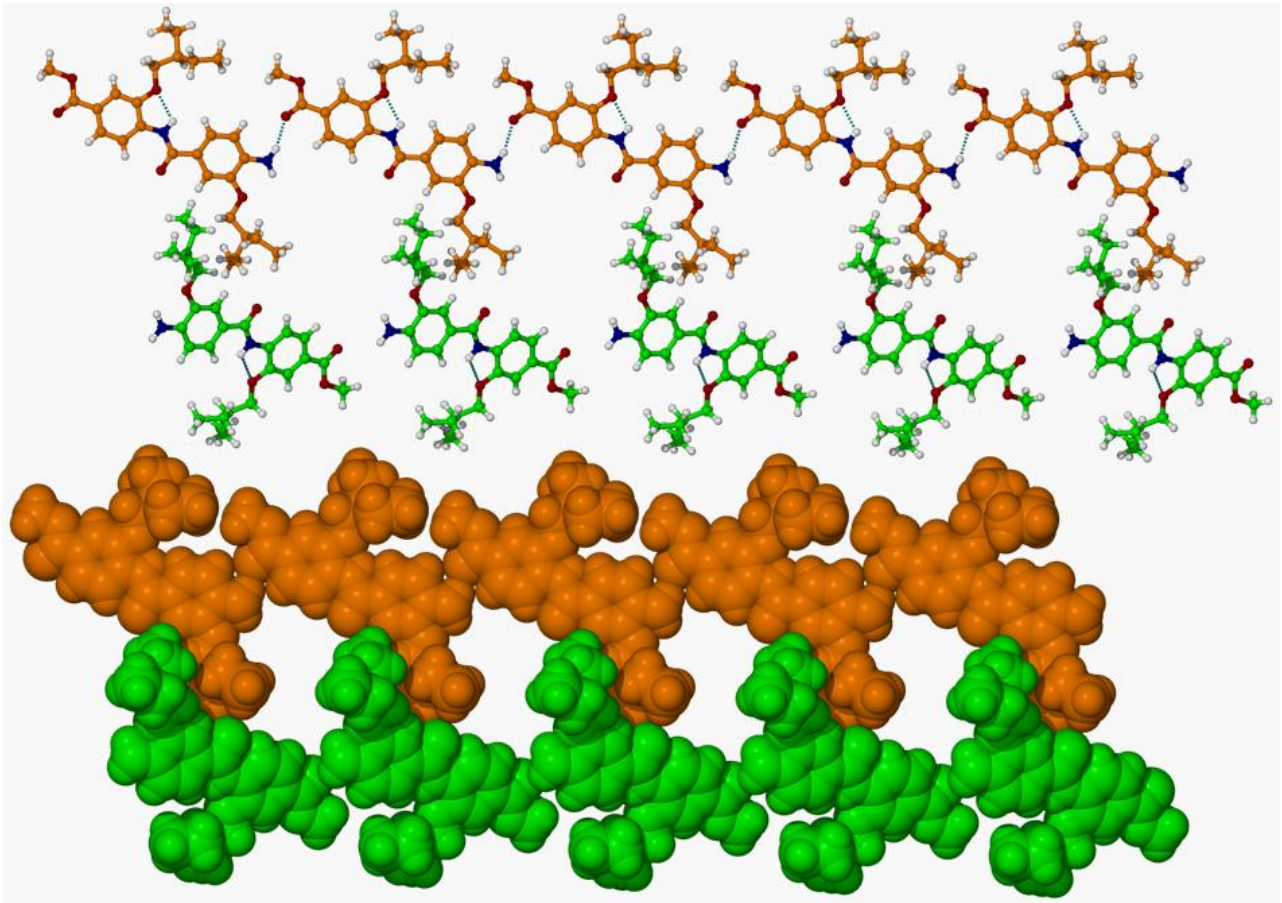

Figure S12. Packing motif of dimer **14c**: hydrophobic interactions of CH_2-3-pentyl side chains connecting the linear networks together, pattern 1 (CPK and ball-and-stick format)

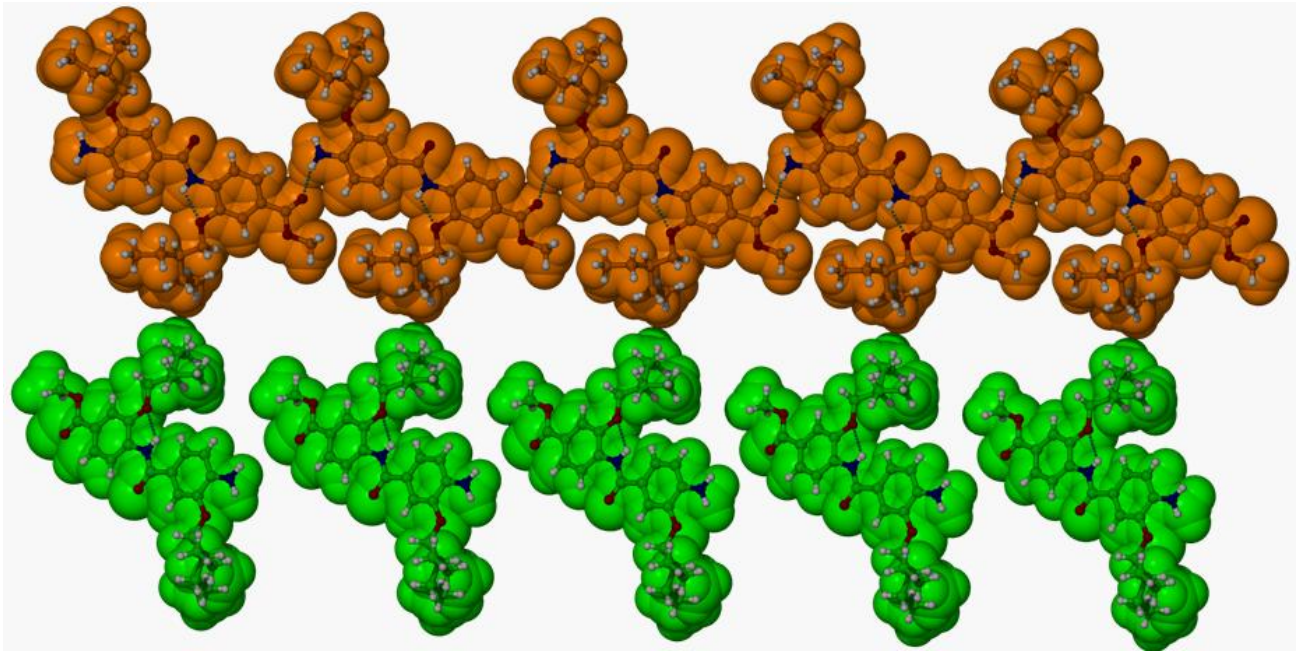

Figure S13. Packing motif of dimer **14c**: pattern 2 (CPK and ball-and-stick format overlay)

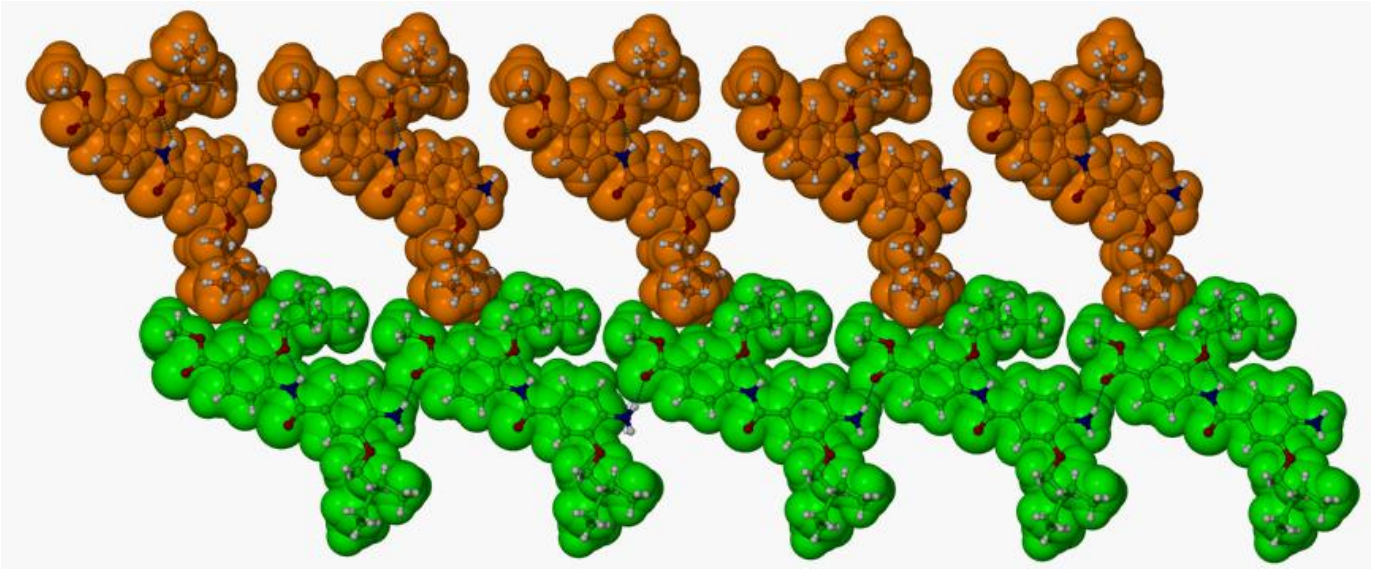

Figure S14. Packing motif of dimer **14c**: pattern 3 (CPK and ball-and-stick format overlay)

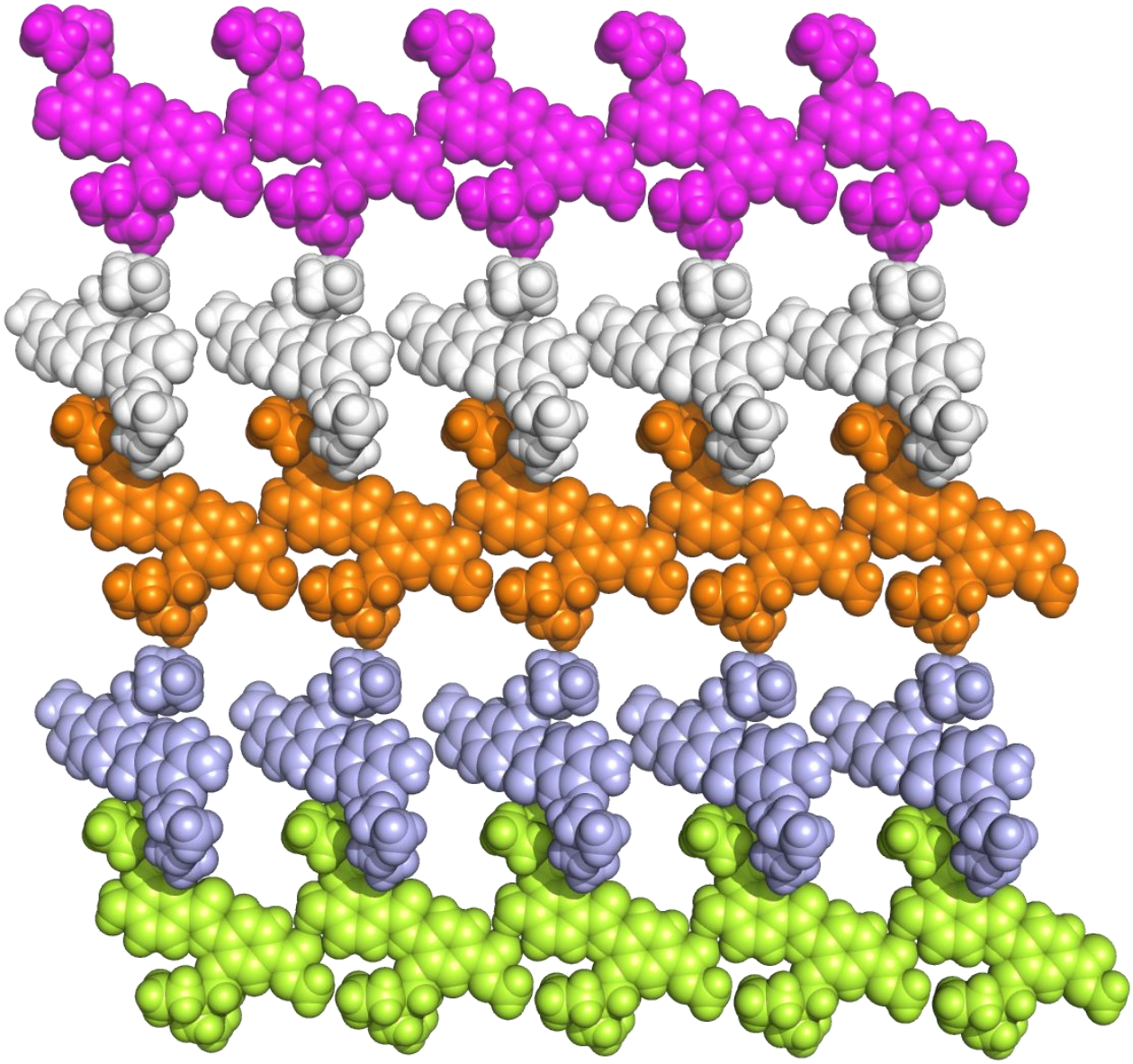

Figure S15. Packing motif of dimer **14c**: formation of molecular sheet from the linear networks (CPK format)

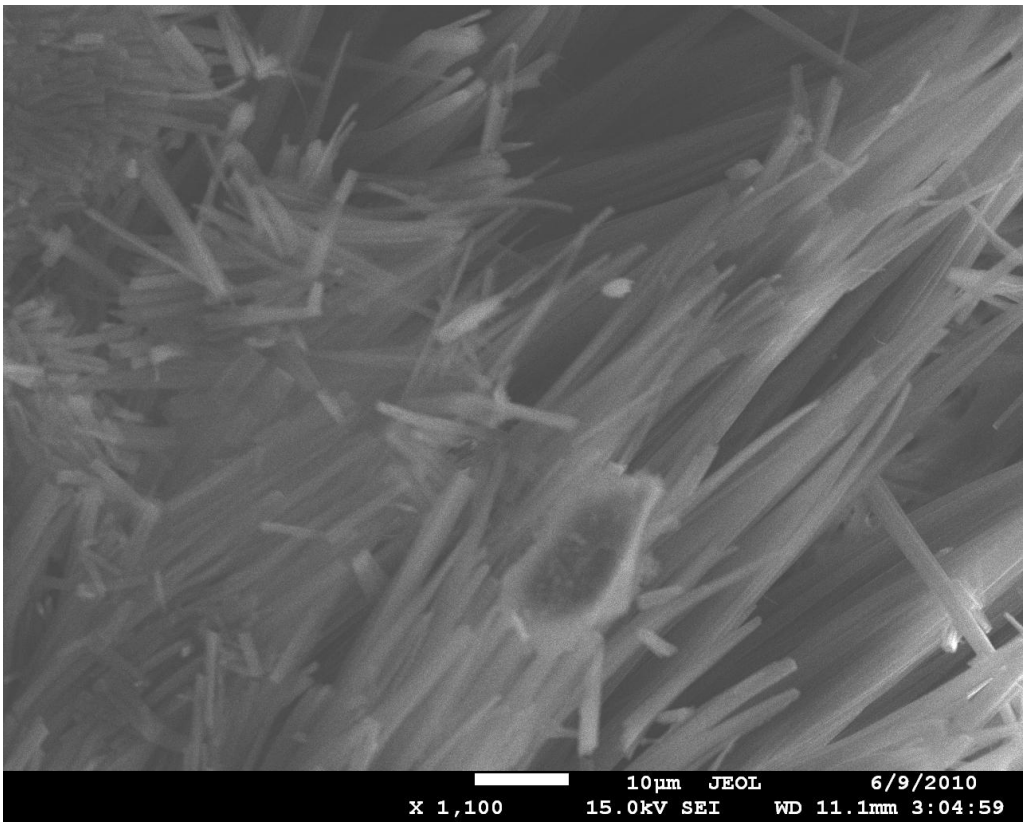

Figure S16. SEI of dimer **6** (magnification x 1,100)

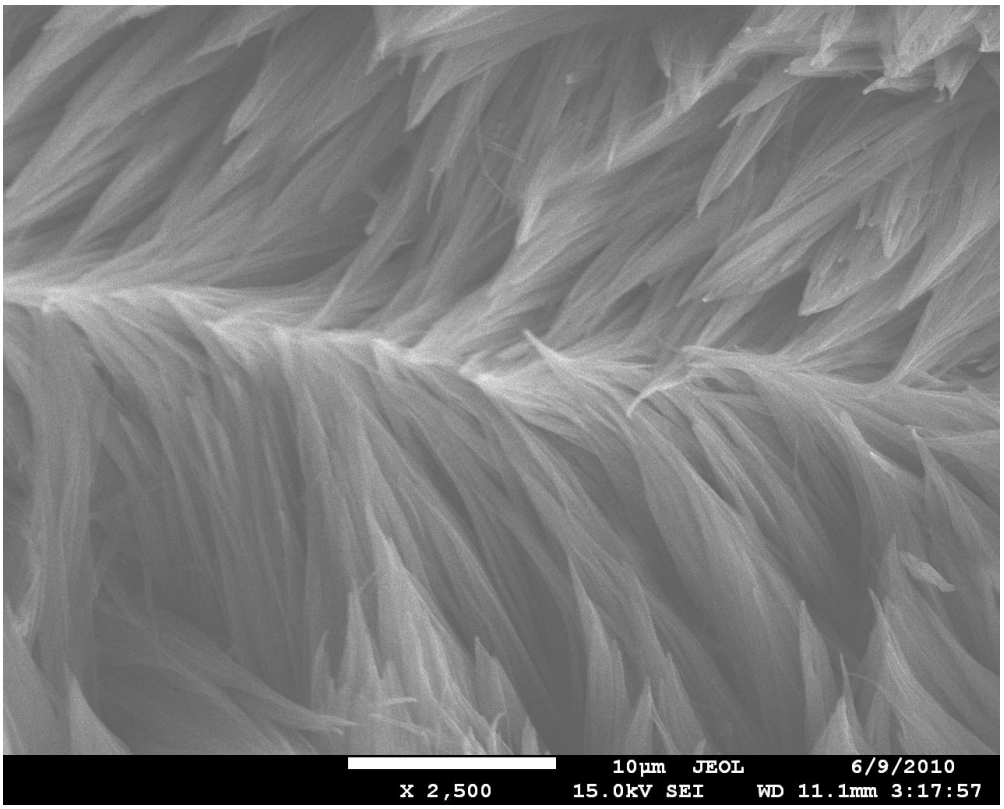

Figure S17. SEI of dimer **6** (magnification x 2,500)

References

11. CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku and Rigaku Americas (2000-2010). 9009 New Trails Dr. The Woodlands TX 77381 USA.
12. SHELX97: Sheldrick, G.M. (1997).